# THE STANDARD ELECTRODE POTENTIAL

# OF

# THE URANOUS-URANYL SULFATE REDOX ELECTRODE

By

Edward Orban

Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

1944





ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
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ACKNOWLEDGMENT

The author wishes to express his deep appreciation to Doctor Malcolm M. Haring for suggesting the problem and for his constant supervision thereof.

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# INTRODUCTION

Very little work has been done since 1908 on the oxidation-reduction potentials of the uranous-uranyl ion system. At that time measurements were made with little knowledge of activity coefficients and their dependence on ionic strength. The results obtained were necessarily approximate, and it is the purpose of this research to redetermine the standard potential of the uranous-uranyl ion system taking into account the present day knowledge of the behavior of ions in solution.

The standard potential of the uranous-uranyl ion system can be obtained by taking measurements of the potentials of cells at various dilutions and extrapolating the results to zero ionic strength where the activity coefficients by definition are equal to unity.

The standard potential of the uranous-uranyl ion system is necessary in the quantitative determination of uranium by electrochemical methods and in the use of uranous and uranyl salts as oxidizing and reducing agents. The relative oxidizing and reducing powers of these two ions should be useful in research concerning the isolation and concentration of uranium from its ores. It is hoped that this research may play some small part in the conquest of atomic powers.

# HISTORICAL REVIEW

In 1889 Nernst (20) showed how electromotive force cells could be treated thermodynamically using ionic concentrations in the solution of the problem. It was not until 1907 that Lewis (13) defined activities which we now know must be used in the Nernst equation in place of concentrations in order to give accurate results.

In 1904 R. Luther and A. C. Michie (18) made an investigation of the oxidation-reduction potentials of an oxidizing agent which depended on the hydrogen ion concentration. Their results at that time did not agree with the theory; therefore, they did not immediately publish them. The cell which they used was:

$$\text{Pt} \;\Big|\; \begin{matrix} U(SO_4)_2 & (zm) \\ UO_2SO_4 & (ym) \\ H_2SO_4 & (xm) \end{matrix} \;\Big|\; H_2SO_4 \quad (xm) \;\Big|\; Hg_2SO_4 \;\Big|\; \text{Hg}$$

In 1908, after Lewis had defined activities, they made measurements to correct for the activities of sulfuric acid, and they published their results to show that they actually did agree with the theoretically calculated values.

There were several factors which they did not account for or did not know about. First of all, although they corrected for the activities of sulfuric acid, they did not attempt to make a correction for the activities of uranous or uranyl salts. Secondly, they eliminated the liquid junction potential of sulfuric acid by maintaining the same acid concentration in each half cell, but they did not eliminate the liquid junction caused by the uranous and uranyl salts. In every cell that they measured, the ratio of sulfuric acid to uranium salts were less than 5 to 1; in fact, in dilute acid solutions the uranium salts concentration was comparable to the acid concentration.

The value that Luther and Michie reported for the standard potential of the uranous-uranyl ion half cell, which undergoes the reaction,

$$UO_2^{++} + 4H^+ + 2e = U^{4+} + 2H_2O,$$

was 0.419 volts positive to the Nernst zero point and 0.696 volts positive to the Ostwald zero point. The Nernst zero point is the potential of a half cell when it is referred to the standard hydrogen electrode, while the Ostwald zero point is the potential of a half cell referred to the normal calomel electrode as the standard. The difference between the two is the potential of the normal calomel electrode referred to the standard hydrogen electrode which was given as 0.277 volts at the time Luther and Michie made their measurements. The standard potentials of half cells now are referred to the standard hydrogen electrode (Nernst zero point) almost exclusively.

R. Gerke (6) recalculated these values using a new value for the standard potential of the reference electrode which Luther and Michie used. He arrived at the value of 0.358 volts for the standard potential of the half cell which he estimated to be good to $\pm$ 0.1 volts. His calculation was made by simply adding the standard potential of the sulfuric acid, mercurous sulfate, mercury half cell to the measured potentials and correcting for the concentrations of the acid and uranium salts. To be

exact he should not have used the standard potential of the reference electrode, but he should have corrected it for the activity of the sulfate radical; moreover, he should have recalculated the effect of the hydrogen ion on the standard potential of the redox half cell using the best possible values of the activity of the hydrogen ion. Calculations made taking these two effects into consideration give 0.491 volts as the standard potential from the measurements of Luther and Michie. This value is still uncorrected for the activity coefficients of the uranous and uranyl ions or for liquid junction potentials.

McCoy and Bunzel (19) measured the potentials of various mixtures of uranous sulfate and uranyl sulfate which analysed as 0.0493 molar total uranium salt concentration and 0.125 molar free sulfuric acid concentration. Their equation:

$$E = E^{\circ} + 0.0298 \log_{10} \frac{C_{UO_2^{++}}}{C_{U^{4+}}},$$

did not account for the hydrogen ion concentration or for the activities of the ions; moreover, they made no attempt to correct for the liquid junction potentials, but they arrived at a value of $E^{\circ} = 0.615$ volts.

Shcherbina (23) gave the oxidation-reduction potential of $U^{4+} \rightleftharpoons U^{6+}$ in 1N solutions at 18°C as +0.41 volts.

Popoff and Kunz (21) eliminated the liquid junction of a ferric-ferrous ion half cell by plotting decreasing concentrations of ferric-ferrous mixtures against the potential of the cell after correcting for the salt concentration and extrapolating to zero salt concentration. The extrapolated value of the potential they called $E_j$. This was repeated for decreasing concentrations of acid. The $E_j$ values for the various acid concentrations were then plotted against the acid molality and again extrapolated to zero ionic strength which gave the true $E_o$

value since at zero strength all of the activity coefficients become equal to unity.

J. E. Carpenter (2) determined that standard potential of the vanidol-vanadyl ion system which is dependant on the acid concentration as is the uranous-uranyl ion system. For his work he used the data of Coryell and Yost (3). He plotted the potential of the cell corrected for the concentrations of salts and acid against the square root of the ionic strength. As the square root of the ionic strength approached zero, the curve approached a horizontal tangent, and the intercept of the y axis gave the true value of the standard potential. A method very similar to this will be used in this research to determine the standard potential of the uranous-uranyl ion system.

## THEORETICAL DISCUSSION

Nernst (20), in 1889, postulated that for a metal immersed in a liquid there is a definite tendency for the atoms of the metal to go into the ionic state as indicated by the following equation:

$$M = M^{+} + e.$$

This tendency is known as the "electrolytic solution pressure", or the "electrolytic solution tension". He stated that the more electropositive an element, the greater the tendency for the metal to give up electrons and form ions. In this way the electropositivity (or electronegativity) of a metal is correlated with the "electrolytic solution pressure". Although the "electrolytic solution pressure" may be high, the number of ions going into solution may be small due to the formation of an electric double layer of ions on the surface of the metal. This is caused by the accumulation of electrons in the metal which exert an electrostatic attraction for the ions.

Another factor influencing the passage of metallic ions into solution is the osmotic pressure of the ions already in the solution. If the osmotic pressure is high, the passage of ions into solution is inhibited. If it is low, the passage is enhanced.

Nernst showed that the electrode potential of a metal could be expressed by the equation:

$$E = \frac{RT}{nF} \ln \frac{P}{\Pi}$$

where P is the "electrolytic solution pressure", $\pi$ is the osmotic pressure, R is the gas constant, F is the Faraday, n is the number of electrons involved, and T is the absolute temperature.

The thermodynamic derivation of the Nernst equation is obtained from a consideration of the free energy change of a cell reaction. For the general cell reaction,

$$aA + bB + \cdots\cdots = yY + zZ + \cdots\cdots, \qquad (1)$$

the free energy change for the substances in any given state can be written:

$$\Delta F = (yF_Y + zF_Z + \cdots\cdots) - (aF_A + bF_B + \cdots\cdots). \qquad (2)$$

The standard free energy change can be written as:

$$\Delta F^\circ = (yF_Y^\circ + zF_Z^\circ + \cdots\cdots) - (aF_A^\circ + bF_B^\circ + \cdots\cdots). \qquad (3)$$

By the method of Lewis and Randall (14) it is possible to combine these two equations and obtain the equation:

$$\Delta F - \Delta F^\circ = RT \ln \frac{a_Y^y \; a_Z^z \cdots}{a_A^a \; a_B^b \cdots}, \qquad (4)$$

by use of the relation:

$$y\,(F_Y - F_Y^\circ) = RT \ln a_Y^y$$

and similar relations for each of the other reactants and products. In this equation a represants the activity which may also be called the *effective* concentration.

The free energy change of a voltaic cell is also given as:

$$\Delta F = -nFE \tag{5}$$

or for the standard state:

$$\Delta F^{\circ} = -nFE^{\circ}. \tag{6}$$

Therefore,

$$nFE - nFE^{\circ} = -RT \ln \frac{a_Y^y a_Z^z \cdots\cdots}{a_A^a a_B^b \cdots\cdots} \tag{7}$$

or

$$E - E^{\circ} = -\frac{RT}{nF} \ln \frac{a_Y^y a_Z^z \cdots\cdots}{a_A^a a_B^b \cdots\cdots} \tag{8}$$

which is the same as:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_Y^y a_Z^z \cdots\cdots}{a_A^a a_B^b \cdots\cdots}$$

The conventions of sign followed are those given by Getman and Daniels (7).

They are as follows:

1. The electromotive force is positive when the cell reaction occuring is spontaneous.
2. The cell is written so that electrons leave the cell at the left and enter at the right.
3. The potential of the half cell is the potential of the whole cell with standard hydrogen half cell at the left.

The oxidation - reduction electrode is commonly thought of as a mixture of two valence states of metal in solution with an inert metal electrode dipping into the solution. Its behavior is similar to the ordinary types of electrodes, and the general reaction may be written as:

$$\text{reduced state} = \text{oxidized state} + n \text{ electrons.}$$

The Nernst equation for this type of electrode is:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$

where n is the number of electrons between the two states, and $a_{ox}$ and $a_{red}$ represent the activities of the oxidized and reduced states respectively.

The cell used for this research may be written as follows:

$$\text{Pt} \;\Big|\; H_2 \;\Big|\; H_2SO_4 \;\; (xm) \;\Big|\; \begin{matrix} H_2SO_4 & (xm) \\ U(SO_4)_2 & (ym) \\ UO_2SO_4 & (zm) \end{matrix} \;\Big|\; \text{Pt}$$

Neglecting the sulfate radical since it appears on both sides, the cell can be written as follows:

$$\text{Pt} \;\Big|\; H_2 \;\Big|\; H^+ \;\; (xm) \;\Big|\; \begin{matrix} H^+ & (xm) \\ U^{4+} & (ym) \\ UO_2^{2+} & (zm) \end{matrix} \;\Big|\; \text{Pt}$$

Since oxidation occurs at the left of the cell and reduction at the right, it is possible to write the reaction for each half cell:

$$H_2 - 2e = 2\,H^+$$

$$4H^+ + UO_2^{2+} + 2e = U^{4+} + 2H_2O$$

For aqueous solutions at 25°C, the value of $\frac{RT}{nF} \ln a$ when converted to Briggsian logs is $\frac{0.05915}{2} \log a$.

The Nernst equation for the hydrogen half cell is then:

$$E_L = E^\circ - \frac{0.05915}{2} \log \frac{a_{H^+}^2}{a_{H_2}} \qquad (9)$$

and for the uranous-uranyl half cell:

$$E_R = E^\circ - \frac{0.05915}{2} \log \frac{a_{U^{4+}} \; a_{H_2O}^2}{a_{UO_2^{2+}} \; a_{H^+}^4} \qquad (10)$$

For the hydrogen half cell the standard potential $E^\circ$ is taken as zero, and the activity of a gas is taken as equal to its pressure in atmospheres. The potential of the hydrogen half cell can be rewritten as:

$$E_L = - \frac{0.05915}{2} \log \frac{a_{H^+}^2}{p_{H_2}} \qquad (11)$$

or

$$E_L = \frac{0.05915}{2} \log p_{H_2} - 0.05915 \log a_{H^+}$$

The potential of the entire cell is the summation of the potentials of the left and right half cells:

$$E_{cell} = E_l + E_r.$$

Combining the two equations:

$$E_{cell} = \frac{0.05915}{2} \log H_2 - 0.05915 \log a_{H^+_{(H_2 \text{ electrode})}}$$

$$+ E^\circ - \frac{0.05915}{2} \log \frac{a_{U^{4+}} \; a_{H_2O}^+}{a_{UO_2^{2+}} \; a_{H^+}^4} \text{ (soln)} \qquad (12)$$

Solving for $E^\circ$:

$$E^\circ = E_{cell} - \frac{0.05915}{2} \log P_{H_2} + 0.05915 \log a_{H^+} \ (H_2 \text{ electrode})$$

$$+ \frac{0.05915}{2} \log \frac{a_{U^{4+}} a^2_{H_2O}}{a_{UO_2^{2+}} a_{H^+}} \ (\text{solution}) \qquad (12)$$

The activity of an ion is related to the molality by the equation:

$$a = \gamma m, \qquad (13)$$

where $\gamma$ is the activity coefficient and m is the molality.

Substituting $\gamma$ m for activity it is possible to arrive at the following equation:

$$E^\circ = E_{cell} - 0.05915 \log P_{H_2} + 0.05915 \log (\gamma_{H^+} m_{H^+}) \ H_2 \text{ (electrode)}$$

$$+ 0.05915 \log a_{H_2O} + \frac{0.05915}{2} \log \frac{\gamma_{U^{4+}} m_{U^{4+}}}{\gamma_{UO_2^{2+}} m_{UO_2^{2+}}} \qquad (14)$$

$$-0.05915 \times 2 \log (\gamma_{H^+} m_{H^+}) \ (\text{solution})$$

Since the molalities of the hydrogen ion concentrations were made the same in both half cells, and the hydrogen ion concentration was over one hundred times as large as the uranium salt concentration, the activity coefficient of the hydrogen ion, which is dependent only on the total ionic strength, can be taken as equal in both half cells.

The above equation can then be further simplified to:

$$E^\circ = E_{cell} - 0.05915 \log P_{H_2} - 0.05915 \log \gamma_{H^+} m_{H^+}$$

$$+ \frac{0.05915}{2} \log \frac{\gamma_{U^{4+}} m_{U^{4+}}}{\gamma_{UO_2^{2+}} m_{UO_2^{2+}}} + 0.05915 \log a_{H_2O} . \qquad (15)$$

Taking separate account of the activity coefficients and molalities:

$$E^\circ = E_{cell} - 0.05915 \log p_{H_2} - 0.05915 \log \gamma_{H^+} - 0.05915 \log m_{H^+} + \frac{0.05915}{2} \log \frac{m_{U^{4+}}}{m_{UO_2^{2+}}} \quad (16)$$

$$+ \frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}} + 0.05915 \log a_{H_2O}.$$

In this equation $E_{cell}$, pH2, $m_{H^+}$, $m_{U4^+}$, $m_{UO_2}2+$ are measurable. Rearranging the equation to place the measurable quantities on the same side and the remaining activity coefficients and the activity of water on the left with $E^\circ$, we obtain:

$$E^\circ - \frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}} + 0.05915 \log \gamma_{H^+} - 0.05915 \log a_{H_2O}$$

$$= E_{cell} - 0.05915 \log p_{H_2} - 0.05915 \log m_{H^+} \quad (17)$$

$$- \frac{0.05915}{2} \log \frac{m_{U^{4+}}}{m_{UO_2^{2+}}}.$$

It was found by Harned and Hamer (10) that the activity coefficient of sulfuric acid increases rapidly as the solution approaches zero molality. In view of this information, it was decided to correct for the activity coefficient of sulfuric acid from the excellent data published by the two authors mentioned. The mean activity coefficient of sulfuric acid was used as the activity coefficient of hydrogen ion since data on the activity of a single ion are open to question.

Rearrangement of the preceding equation gives:

$$E^\circ - \frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}} - 0.05915 \log a_{H_2O}$$

$$= E_{cell} - 0.05915 \log P_{H_2} - 0.05915 \log m_{H^+} \qquad (18)$$

$$- 0.05915 \log \gamma_{H^+} - \frac{0.05915}{2} \log \frac{m_{U^{4+}}}{m_{UO_2^{2+}}}$$

The activity coefficient and molality of water may be considered separately to determine their effect on the potential of the cell. The molality of water is always constant and its effect is lumped into $E^\circ$ of the uranous-uranyl electrode. The activity coefficient of water may be corrected for by use of Harned and Hamer data given in the same journal article previously mentioned; or it may be allowed to remain in the equation as an undetermined quantity since, according to Lewis and Randall (14), the activity coefficient of the solvent becomes unity in an infinitely dilute solution; or it may be neglected since the correction in even the most concentrated solution used in this research is well within the experimental error.

P. Debye and E. Huckel (4) were able to show that the activity coefficient of a substance in dilute solution is dependant only on the ionic strength, $\mu$. Furthermore, as the ionic strength approaches zero, the activity coefficient becomes equal to unity; therefore, it is obvious that if a plot of the right side of equation (18) is made against the ionic strength or the square root of the ionic strength, the extrapolation of the curve to zero ionic strength will of necessity be equal to $E^\circ$.

The ionic strength of a solution is calculated by means of the equation:

$$\mu = 1/2 \sum z^2 c^2 \qquad (19)$$

where C is the molality, and z is the valence.

From the value of $E^\circ$ it is possible to calculate the value of $\Delta F^\circ$, the standard free energy change, by means of equation (6). By use of the following equation:

$$\Delta F^\circ = -RT \ln K, \tag{20}$$

the equilibrium constant, K, for the reaction,

$$H_2 + UO_2SO_4 + H_2SO_4 = U(SO_4)_2 + 2H_2O,$$

can be calculated since the standard potential of the hydrogen electrode is equal to zero.

Combining equation (20) with equation (6):

$$E^\circ = \frac{RT}{nF} \ln K \tag{21}$$

which gives the following equation in aqueous solution at 25°C:

$$E^\circ = \frac{0.05915}{2} \log K. \tag{22}$$

The ratio of the activity coefficients at the concentrations used in this research can be calculated from equation (18) since the value of $E^\circ$ has been determined. The value of the right side of the equation is the $E^{\circ\prime}$ value, and the difference between $E^\circ$ and $E^{\circ\prime}$ is the value of

$$\frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}}$$

or expressed as an equation:

$$E^\circ - \frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}} = E^{\circ\prime}.$$

Rearranging:

$$E^\circ - E^{\circ\prime} = \frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}}.$$

Solving for the ratio of the activity coefficients:

$$\frac{f_{U^{4+}}}{f_{UO_2^{2+}}} = \text{anti log } \frac{2(E^\circ - E^{\circ\prime})}{0.05915} . \qquad (23)$$

The ratio of the activity coefficients is necessary for the exact calculation of the potential of a uranous-uranyl half cell from the standard potential of the half cell when used over the same range of concentrations that were measured in this research.

If the values of the mean activity coefficient of either one of these ions are ever determined at the same concentrations that we measured, it will be a simple matter to calculate the activity coefficient of the other ion.

The free energy change, $\Delta F$, can be calculated from the E value of any cell by use of equation (5).

## PROCEDURE

### Apparatus

Hydrogen for the hydrogen electrode was first bubbled through the saturater, D, shown in figure 1, where it became saturated with water vapor at the same partial pressure as that of the solution. This was necessary in order not to change the concentration of the acid solution in the hydrogen electrode, C, when hydrogen passed through it. The hydrogen from the saturater was led into the bottom of the hydrogen cell by means of an inner seal and allowed to bubble up through the solution around two palladinized platinum electrodes. A bubbling tube to prevent the entrance of air into the hydrogen half cell was placed through the same stopper as the two electrodes. The stopcock in the arm prevented any pumping action of the acid when hydrogen was bubbling and was opened only when the hydrogen was turned off for a reading.

To plate the palladium on the palladinized platinum electrode, the electrode was made positive until all of the old palladium plate was stripped off. The platinum foil electrode was saturated with hydrogen and cathodized in a 3% palladium chloride solution for 60 seconds at 150 ma. It was then washed and saturated with hydrogen again for 30 seconds after which it was washed again and placed in the cell. Most of the hydrogen diffused off during the evacuations of the cell to remove the air, but to prevent the remaining traces of hydrogen from causing serious changes in uranium salt concentration, measurements with freshly plated electrodes were first made on concentrated solutions, where the effect of the hydrogen would be negligible. A palladinized platinum electrode was good for about 7-10 cells before it became poisoned and had to be replated.

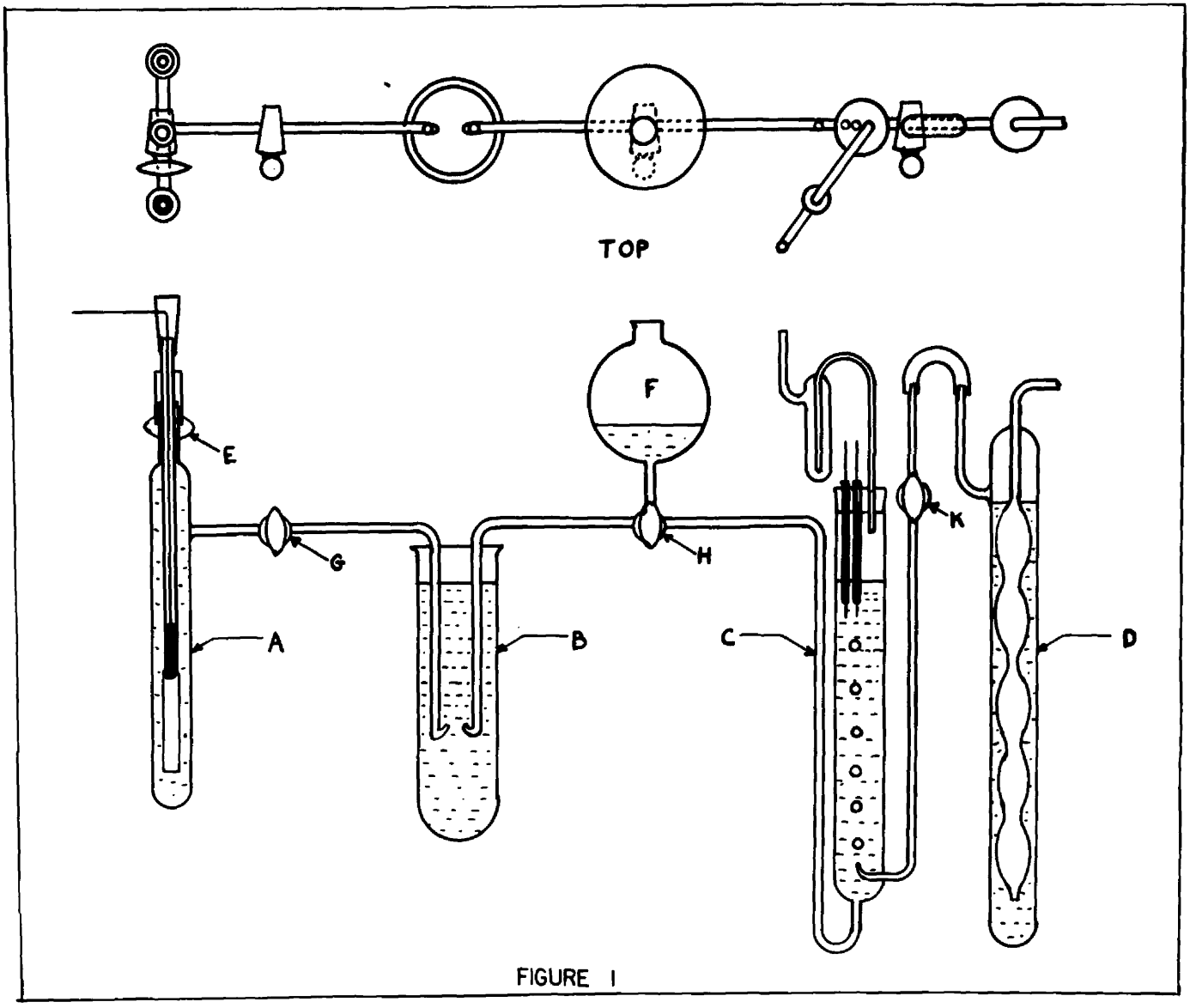
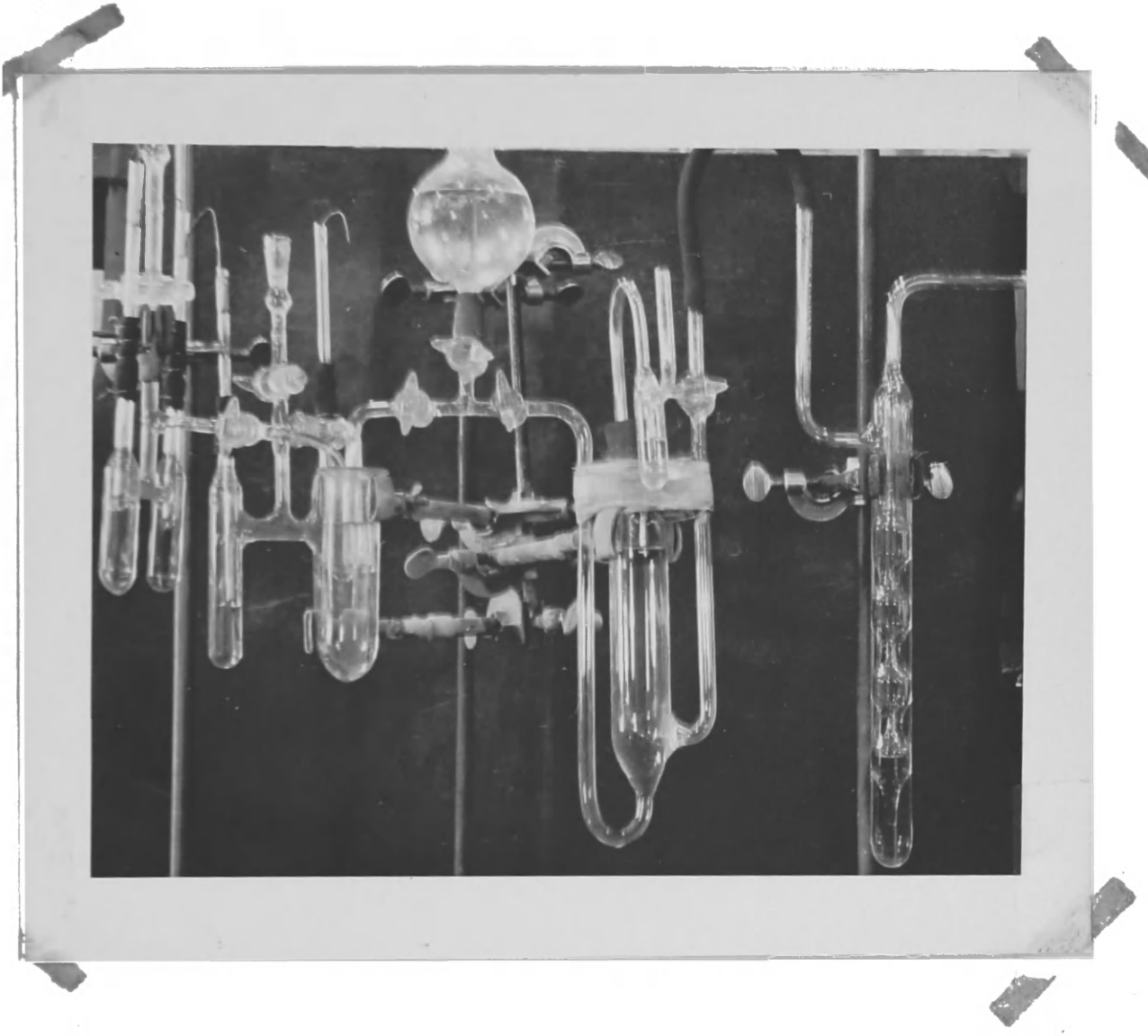



FIGURE 1

Photograph 1.



CELL USED TO MEASURE THE POTENTIALS
(See Fig. 1.)

Two H cells, A in figure 1, were used for each solution measured, and each arm of the cell contained a palladinized platinum electrode which was sealed in by means of a wired rubber slip joint. A small bulb, F, was placed in the ground glass joint as shown in figure 2 when the cell was to be filled with solution. This bulb was removed during measurements to avoid overcrowding the thermostat.

The H cells and the hydrogen cell were bridged by means of a test tube, B in figure 1, which contained acid solution of the same concentration as the cells.

A system for handling solutions in an oxygen free atmosphere had to be devised since oxygen is easily reduced by the uranous ion. The apparatus used is shown diagramatically in figure 2. Whenever a solution of water was to be placed into a flask, the flask was first evacuated by an efficient water pump and filled with oxygen free nitrogen. This process was repeated at least four times in order to insure complete removal of oxygen. Water and a stock solution of known concentration of uranous, uranyl, and hydrogen ions were kept in the two large flasks, G and F respectively. The mixing flask, D, was made so that it could be attached to the other two flasks and filled with nitrogen, and so that solution and water could be transferred into it without admitting any air.

The nitrogen used to fill all the flasks was passed through a small furnace, B, that contained copper gauze heated to a temperature of 450°C. Any traces of oxygen in the nitrogen reacted with the hot copper and were removed. To prevent the ground joints from blowing apart while adding nitrogen to an evacuated flask, a safety valve, C, was introduced into the system to allow the escape of nitrogen when the pressure became higher than a small hydrostatic head.

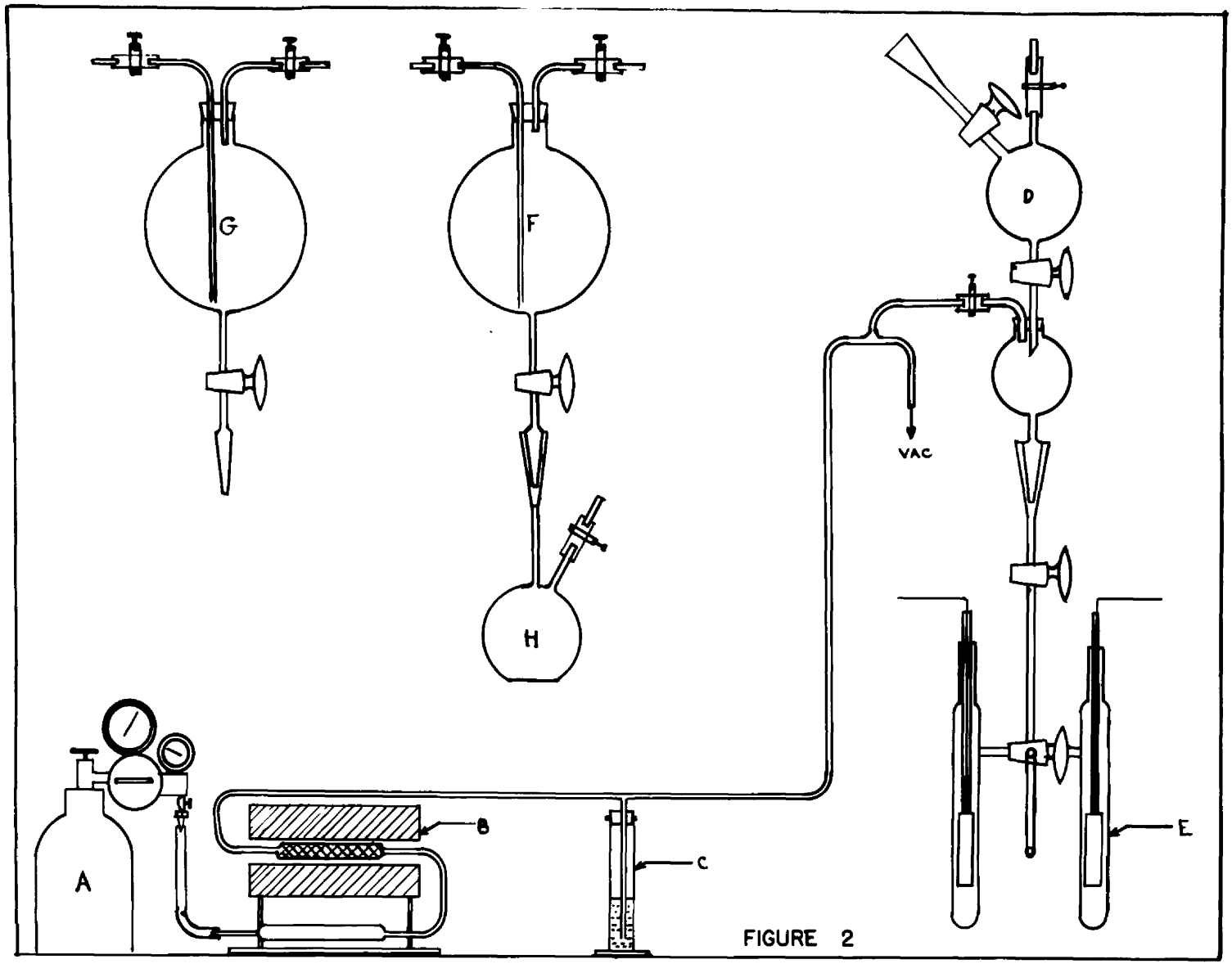
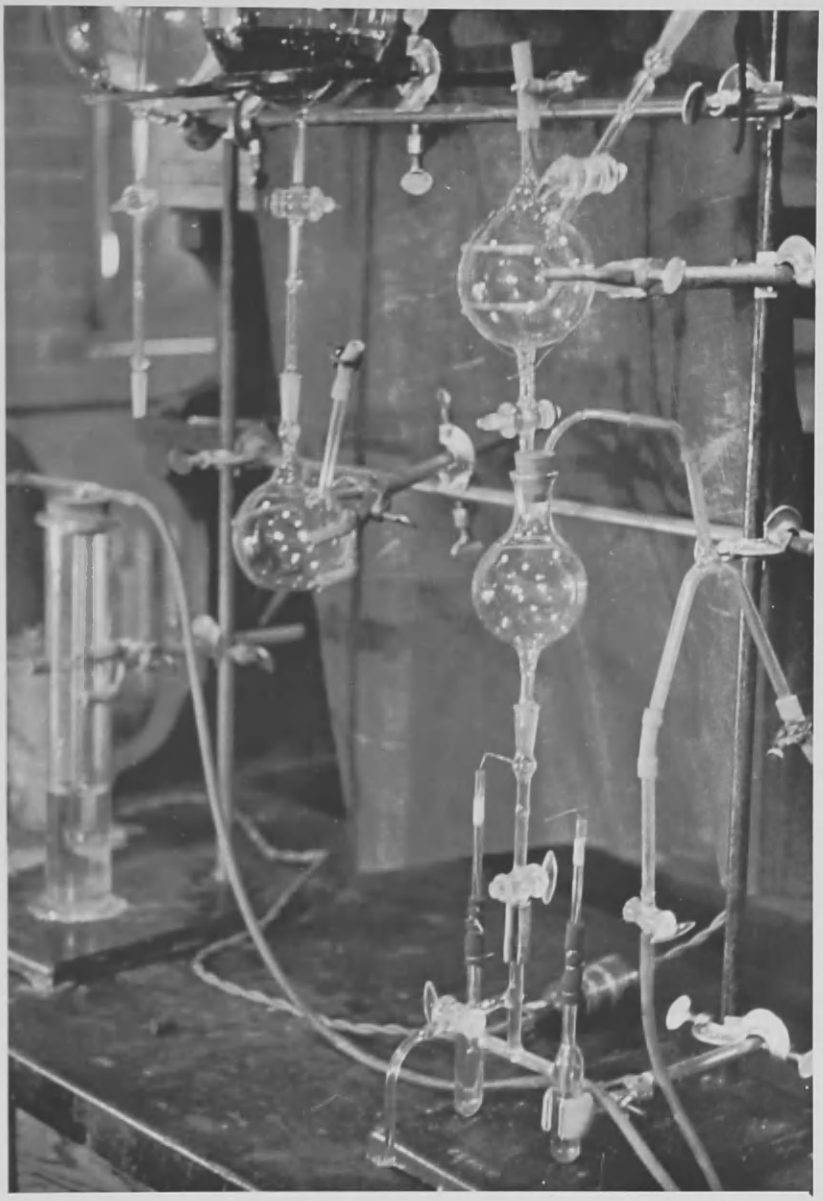



FIGURE 2

Photograph 2.



APPARATUS TO FILL REDOX CELL WITH SOLUTION
(See Fig. 2.)

Photograph 3.

STORING AND ANALYSIS FLASKS
(See Fig. 2. )

The cells were placed in an American Instrument Thermostat bath filled with water that was held at 24.92° ± 0.02°C. Since the thermal regulator was difficult to set and the change in potential caused by 0.10°C variation in temperature was well within experimental error (see discussion of errors), the measurements were made at this temperature rather than at 25°C. Four jacketed burettes were connected in series with the thermostat and a small circulating pump enabling titrations to be made at constant temperature; hence, corrections due to temperature changes were avoided.

A Type B Rubicon potentiometer was used to measure the potentials of the cell, and a Willard L. D. Cell was used as a source for the working current. An Eppley Standard Cell which produced an electromotive force of 1.01867 volts was used as the standard potential. A Leeds and Northrup Type R galvanometer with a sensitivity of 0.003 microamps per mm and with an external critical damping resistance of 2000 ohms was used. A Leeds Northrup lamp and scale was used to detect the deflections of the galvanometer. It was possible to measure the potential of any pair of electrodes through a switchboard and a suitable arrangement of jacks. For each setup a total of eight measurements was made.

The weights and volumetric glassware were calibrated, and all weights were corrected to vacuo. The solutions were all prepared by weight using a Christian Becker Style 14-2 kilogram balance. The balance used for weighing small quantities of materials, such as for standardizing solutions, was a Style 9 - Regular Christian Becker balance. To prevent contamination of the solutions with sulfur which might in turn poison the electrodes, all rubber stoppers and connections were boiled for five minutes in 20% alkali.

# PROCEDURE

## Materials

Uranyl sulfate and uranous sulfate were prepared from uranyl acetate (Mallinckrodt- Analytical Reagent). The preparation of uranyl sulfate was carried out in the same way that Vanino (24) suggests making uranyl sulfate from uranyl nitrate. After all the acetic acid formed had been removed, the concentrated sulfuric acid was removed by continuing to heat until no more fumes were evident. Some of the uranyl sulfate had been reduced to uranous sulfate by the acetic acid first formed; hence, it was necessary to add water and evaporate the solution to dryness several times so that the air could reoxidize any uranous sulfate formed back to uranyl sulfate. The residue was dissolved in a minimum volume of water, and then twice this volume of alcohol was added. Uranyl sulfate is only slightly soluble in a 60% alcohol solution; hence, it was precipitated out. The crystals were then taken up in a small quantity of hot water and allowed to crystallize out in the form of $UO_2SO_4 \cdot 3H_2O$.

The uranous sulfate was prepared directly from uranyl acetate by a method similar to that used by G. N. Wyrouboff (25). Uranyl Acetate was mixed with concentrated sulfuric acid and heated until fumes of $SO_3$ appeared. A small portion of alcohol (25 cc per 50 gms. of uranyl acetate) was added when the solution had cooled. The solution was reheated for several hours until it became a deep green color. The green residue which formed during heating was dissolved by adding small portions of water until it just went into solution. To this solution 95% alcohol was added until no further precipitate was formed on the continued addition of alcohol. The precipitate was filtered, dissolved in dilute sulfuric acid to prevent hydrolysis, and reprecipitated with alcohol. This procedure was repeated twice,

and the final product was heated to 200°C to drive off any remaining alcohol and then stored over calcium chloride. Analysis of this compound showed that it contained 81.6% uranous sulfate which corresponds to a formula of about $U(SO_4)_2 \cdot 6H_2O$; whereas, Wyrouboff reported the compound formed as $U(SO_4)_2 \cdot 8H_2O$. No mention is made of the time of heating or the conditions under which he stored the material so this may be the reason for the variation in composition. No analysis was made of the final product for uranyl content, but the first analysis of the stock solutions indicated that it was small since the determined values of the uranyl ion concentration agreed well with the calculated values.

An attempt was made to produce sulfate by the method of F. Giolitti and G. Bucci (8), which consists of placing a mixture of 1 g. of $UO_2SO_4$, 12 g. of $H_2O$, 6 g. of alcohol, and 4 g. of $H_2SO_4$ in direct sunlight. There was no evidence of a green color due to uranous sulfate after 2 days; therefore, the attempt was abandoned. The solution was not titrated to determine the presence of any uranous ion.

The sulfuric acid used to make the stock solution was purchased from the General Chemical Company and was Analytical Reagent.

A stock solution of sulfuric acid was prepared which was approximately 1.2 molal and was exactly standardized by use of the potassium iodate method of standardizing acids (11). The specific gravity of the solution was measured with a pycnometer.

From weighed amounts of a stock solution of sulfuric acid and solid uranous and uranyl salts, two separate stock solutions of uranium salts in known acid concentration were prepared. Deoxygenated nitrogen was blown through these solutions for two hours in order to rid the solution of as much oxygen as possible. They were allowed to stand several days to insure complete reaction of any remaining oxygen with uranous

sulfate.

To determine the concentration of the uranous sulfate in the mixture, a sample of solution was allowed to run into the sample flask, H in figure 2, which had been previously filled with nitrogen. This sample was weighed and immediately titrated with 0.025 N potassium permanganate prepared from 0.1 N potassium permanganate that had been standardized with Sörensen's Primary Standard sodium oxalate.

The uranyl sulfate concentration was obtained by determining the total uranium concentration and subtracting the uranous concentration previously found. To determine the total uranium concentration, a weighed sample was run through a Jone's Reductor according to the directions of Kolthoff and Sandell. (11)

The solutions being titrated for total uranium content and uranous content were titrated with 0.025 N potassium permanganate using Orthophenanthrolene-Ferrous Complex as an indicator since the permanganate solution was too dilute to act as its own indicator.

Each stock solution was diluted to give uranium salt solutions of known concentrations. The cells marked with the asterisk in tables 3 and 4 were prepared from stock solution 2, while the unmarked ones were prepared from solution 1. In plates 1 and 2 the black circles indicate measurements of cells prepared with stock solution 2; whereas, white circles indicate measurements of cells prepared from stock solution 1.

The sulfuric acid for the hydrogen half cell was made to exactly the same hydrogen ion molality as the uranium salt solution by adding an exact quantity of water to a known weight of stock acid solution.

Hydrogen and nitrogen were obtained from the Southern Oxygen Company. The nitrogen was oil pumped and contained considerable quantities of oxygen.

It was necessary to reduce the copper oxide formed in the furnace after two hours constant use when the rate of flow was about two bubbles a second through water. Hydrogen was purified by passing it through a furnace containing platinum gauze heated to 200°C. Any oxygen present united with hydrogen and was removed in the form of water vapor.

## Procedure

### Experimental Details

Attempts were first made to ascertain which type of electrode would be best suited for the uranous-uranyl ion solution. Luther and Michie (17) reported that platinized platinum electrodes attained equilibrium very rapidly, while smooth platinum electrodes drifted toward equilibrium very slowly.

A run was made in which two palladinized platinum electrodes were used versus two smooth platinum electrodes. The palladinized electrodes came to equilibrium very rapidly; whereas, the smooth platinum electrodes drifted very slowly in the direction of equilibrium. Platinized platinum electrodes were not tried since they are more difficult to plate and are more sensitive to poisons than palladinized platinum electrodes. In solutions of concentration greater than 0.001 molal total salt, the palladinized platinum electrodes came to equilibrium with a previously saturated hydrogen electrode in one-half hour without the use of a promoter. Carpenter (2) found that traces of $FeCl_3$ behaved as a promoter for the attainment of equilibrium in his work on concentrated vanidol-vanadyl ion systems, but that they were unnecessary in dilute solutions.

In very dilute solutions agreement between palladinized platinum electrodes was not so good as in concentrated solutions; therefore, an attempt was made to use mercury electrodes prepared with distilled mercury because the surface could be easily reproduced. The mercury electrodes produced unsatisfactory results in that they were 0.3 volts higher than the palladinized platinum electrodes and did not agree with each other. It was thought that some overvoltage phenomena was occuring at the surface which

prevented the electrodes from reaching a true equilibrium value.

In the first attempt to standardize the uranium salt solution for uranous salt content, it was found that no consistent result could be obtained. The analyses were run on a solution of approximately 0.01 molal $U(SO_4)_2$ and 0.01 molal $UO_2SO_4$ that was exposed to air in a volumetric flask but was not shaken. The runs were made at intervals of about 10 minutes and the following results were obtained:

Table 1.

| Sample No. | g. of $U(SO_4)_2$ / g. of soln. |
|---|---|
| 1. | 0.007495 |
| 2. | 0.007503 |
| 3. | 0.007447 |
| 4. | 0.007427 |
| 5. | 0.007357 |
| 6. | 0.007328 |
| 7. | 0.007262 |
| 8. | 0.007239 |
| 9. | 0.007239 |

The close agreement between the last two analyses is due to the exclusion of air by bubbling deoxygenated nitrogen through the solution and to the great hurry with which the solution was run.

To determine the effect of air on dilute solutions of uranous sulfate in actual cells, a cell was prepared in which the air was not removed. Over a period of 15 hours the change of potential of the cell was 0.56 volts. This indicated a change in ratio of uranous ion to uranyl ion from 0.74 to 1 at the start to a ratio of 1 to $1 \times 10^{19}$ after 15 hours. The total exposed surface area was 6 square centimeters.

These results were surprising since Lundell and Knowles (17) reported that they found the uranous ion very stable to air; however, their measurements were made in the absence of any uranyl ion, and the results of an experiment determining the total uranium content of a solution confirmed

their observation. After all the solution had been run through a Jones Reductor, it was assumed that the reduction was complete and no uranyl ions remained. Next it was necessary to bubble air through the solution to reoxidize ions of the lower valence states of uranium up to the uranous state. Various bubbling times were tried and the following results were obtained:

Table 2.

| Time of bubbling | g. of $U(SO_4)_2$/g. of soln. |
|---|---|
| 3 minutes | 0.009850 |
| 6 minutes | 0.009867 |
| 12 minutes | 0.009866 |

These results show that there was no reoxidation of the uranous ion to uranyl by bubbling air through the solution; and they lead one to the conclusion that the uranyl ion has a definite catalytic effect on the oxidation of the uranous ion by air.

The apparatus shown in figure 2 was constructed to handle solutions in the absence of air from the time they were made from the stock solution and water until they were sealed in the cell.

The weighed mixing flask, D, was attached to the flask, F, which contained the stock solution of uranium salts, by means of a ground glass joint which was lubricated around the top to prevent the leakage of air into the flask. After the cell had been filled with deoxygenated nitrogen, as described under the description of the apparatus, an estimated amount of solution was allowed to be drawn into the flask under a vacuum. Flasks D and F were then refilled with nitrogen and flask D was reweighed.

It was then attached to flask G, in the same manner as it had been attached to flask F, and an estimated amount of water was allowed to run into it. Flasks D and G were filled with nitrogen, and flask D was again weighed. From the known concentrations of the stock solution and the amount of water added, it was possible to calculate the molalities of the uranous, uranyl, and hydrogen ions of the solution in flask D.

Knowing the exact hydrogen ion molality of the uranium salt solution, an acid solution of the same molality was prepared for the hydrogen half cell by weighing out some of the standardized acid solution in a volumetric flask. To this solution the exact weight of water necessary to make the molalities of the two solutions exactly the same was added by means of a pipette.

To transfer the solution from flask D to the oxidation-reduction chamber E, the apparatus was arranged as shown in figure 2. The chamber was evacuated through the bulb at the top and filled with nitrogen as described previously. The solution was then drawn into the chamber and closed to the air by means of the stopcock.

The hydrogen electrode chamber, C in figure 1, was rinsed with acid solution and filled in the ordinary manner. The two electrodes and the bubbler, which contained the same acid solution as the chamber, were held in place by means of a rubber stopper. The saturater, D, was filled with acid solution, and the hydrogen was allowed to pass through this solution first in order that the hydrogen could become saturated with water vapor and not change the concentration of hydrogen ion in the chamber by absorbing out some of the water. The bulb, F, was filled with acid in order to have a reservoir from which to raise and lower the level of acid solution in the electrode chamber or in the acid bridge, B, which connected the redox half cell with the hydrogen half cell. The level of solution in

chamber C and in the acid bridge had to be the same in order to prevent any syphoning effect.

The hydrogen half cell and acid bridge were prepared first and placed in the thermostat bath which had been previously adjusted to 24.92°C. Hydrogen was bubbled into the hydrogen half cell while the redox half cells were being prepared. By the time the redox half cells were placed in the bath, the hydrogen half cell was nearly saturated with hydrogen.

Cells were allowed to remain in the thermostat until equilibrium was attained. The more concentrated solutions reach equilibrium in one-half to one hour, while the dilute solutions required from one hour to three days depending on the concentration. When the potential of the cell no longer drifted but remained constant for a period of at least four hours, the value was taken as the equilibrium value.

Some 49 cells were prepared over a range from 0.0002 molal to 0.005 molal uranium salt. The first eight cells were discarded since the results obtained were not made under air free conditions. Other cells were discarded when it became obvious that the electrodes were not going to come to equilibrium or when traces of air had been admitted at any time during the preparation.

The water used to dilute the solutions was boiled for five minutes, poured into a storing flask, and nitrogenated until cool.

Table 3 shows the hydrogen ion concentration of both solutions used to prepare the cells, the activity coefficient of the hydrogen ion, and the potentials measured for the thirty-five cells which gave equilibrium values.

TABLE 3.

| | Molality of $H^+$ ($H_2$ electrode) | Molality of $H^+$ (solution) | Act. Coef. of $H^+$ | Meas. Potential |
|---|---|---|---|---|
| 1.* | 0.00734 | 0.00734 | 0.680 | 0.2821 volts |
| 2.* | 0.00763 | 0.00756 | 0.674 | 0.2835 " |
| 3. | 0.01072 | 0.01078 | 0.628 | 0.2929 " |
| 4. | 0.01339 | 0.01343 | 0.600 | 0.2950 " |
| 5. | 0.01355 | 0.01362 | 0.597 | 0.2961 " |
| 6. | 0.01599 | 0.01609 | 0.576 | 0.2999 " |
| 7.* | 0.01710 | 0.01710 | 0.568 | 0.2982 " |
| 8. | 0.02253 | 0.02266 | 0.530 | 0.3069 " |
| 9.* | 0.02686 | 0.02686 | 0.507 | 0.3082 " |
| 10. | 0.02735 | 0.02738 | 0.502 | 0.3112 " |
| 11. | 0.03138 | 0.03157 | 0.486 | 0.3149 " |
| 12. | 0.03175 | 0.03195 | 0.485 | 0.3148 " |
| 13.* | 0.03759 | 0.03759 | 0.463 | 0.3156 " |
| 14. | 0.03931 | 0.03937 | 0.455 | 0.3185 " |
| 15.* | 0.04546 | 0.04519 | 0.438 | 0.3185 " |
| 16. | 0.05000 | 0.05020 | 0.425 | 0.3246 " |
| 17.* | 0.05410 | 0.05319 | 0.416 | 0.3231 " |
| 18. | 0.05361 | 0.05391 | 0.416 | 0.3265 " |
| 19.* | 0.06409 | 0.06409 | 0.394 | 0.3283 " |
| 20.* | 0.07357 | 0.07410 | 0.378 | 0.3354 " |
| 21. | 0.07466 | 0.07477 | 0.377 | 0.3346 " |
| 22.* | 0.07994 | 0.08048 | 0.369 | 0.3371 " |
| 23.* | 0.08289 | 0.08303 | 0.363 | 0.3326 " |
| 24.* | 0.08444 | 0.08475 | 0.361 | 0.3361 " |
| 25. | 0.09766 | 0.09772 | 0.343 | 0.3408 " |
| 26.* | 0.1105 | 0.1027 | 0.327-.337 | 0.3392 " |
| 27. | 0.1196 | 0.1203 | 0.317 | 0.3466 " |
| 28. | 0.1215 | 0.1223 | 0.314 | 0.3469 " |
| 29.* | 0.1324 | 0.1324 | 0.302 | 0.3456 " |
| 30. | 0.1458 | 0.1464 | 0.291 | 0.3510 " |
| 31.* | 0.1658 | 0.1658 | 0.277 | 0.3509 " |
| 32. | 0.1927 | 0.1940 | 0.265 | 0.3586 " |
| 33.* | 0.1933 | 0.1921 | 0.265 | 0.3537 " |
| 34. | 0.2075 | 0.2086 | 0.262 | 0.3587 " |
| 35.* | 0.2607 | 0.2607 | 0.246 | 0.3621 " |

* These solutions were made from stock solution 2.

## DISCUSSION OF RESULTS

### Calculation of Results

The pressure of hydrogen must be taken into account in the calculation of the potential of the hydrogen electrode. From the equation for the reaction of the hydrogen half cell;

$$H_2 = 2H^+ + 2e$$

the equation for the potential of the hydrogen half cell is:

$$E = \frac{0.05915}{2} \log \frac{a_{H^+}}{P_{H_2}} . \qquad (11)$$

The pressure of hydrogen in atmospheres is always used in this equation. Since the hydrogen is passed through the solution, the vapor tension of water must be subtracted from the total pressure over the solution. The total pressure over the solution was the sum of the barometric pressure and a small hydrostatic head in the trap at the top of the hydrogen half cell which amounted to 2-5 mm of water. The corrections to the measured potentials for the pressure of hydrogen are listed in table 4.

The values of the activity coefficients were obtained from a large graph prepared from the values of the activity coefficients by Harned and Hamer (10) at various acid concentrations. Table 4 shows the correction due to the molality and the activity coefficient of the hydrogen ion. In most cases where the molalities of the hydrogen electrode differ from the molality of the redox electrode, they are close enough so that no difference in the activity coefficient can be read from the graph. Where there is a difference in activity coefficients, the activity coefficients of both sides are given and are taken into account in the final correction.

It was not necessary to determine the correction to the measured

potential for the molalities of uranyl and uranous salts in each diluted solution. The ratio of the molalities of the uranous and uranyl salts remains constant on dilution since both molalities are taken only to the first power. The ratio of the molalities was determined for the stock solution, and this ratio was used to calculate the correction to the potential due to the molalities of the two salts. Analyses of the uranous sulfate content were made every two weeks, and the change in concentration during the two weeks was found to be a linear function of the time. From the analyses of the stock solution and from the time between the analyses and the preparation of the diluted solution it was possible to calculate the exact concentration of uranous and uranyl ions at the time the solution was prepared. The oxidation of uranous sulfate to uranyl sulfate liberates hydrogen ions, and the increase of concentration of acid can be calculated from the decrease of concentration of uranous ion. The correction to the potential of the half cell due to the concentration of uranous and uranyl ions is shown in table 4.

The ionic strength also shown in table 4 was calculated by means of equation (19).

In order to determine the value of $\frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}}$, it is necessary to take measurements in extremely dilute solutions or to extrapolate values obtained in more concentrated solutions to the value at zero ionic strength. In a solution of zero ionic strength, the activity coefficient of any salt is unity; hence, if the values of the right side of equation (18) are extrapolated to zero ionic strength, the ratio of the activity coefficients of uranyl and uranous salts should become equal

Table 4. **

| | $0.05915 \log m_{H^+}$ ($H_2$ electrode) | $2.0.05915 \log m_{H^+}$ (solution) | $\frac{0.05915}{2} \log \frac{m_{U^{4+}}}{m_{UO_2^{2+}}}$ | $0.05915 \log p_{H_2}$ | $0.05915 \log \Gamma_{H^+}$ | $E^{\circ\prime}$ | ionic strength | $\sqrt{\text{ionic strength}}$ |
|---|---|---|---|---|---|---|---|---|
| 1.* | 0.1263 | 0.2526 | 0.0039 | 0.0002 | 0.0099 | 0.4146 | 0.0120 | 0.1097 |
| 2.* | 0.1252 | 0.2509 | 0.0036 | 0.0004 | 0.0101 | 0.4161 | 0.0124 | 0.1114 |
| 3. | 0.1165 | 0.2327 | 0.0063 | 0.0003 | 0.0120 | 0.4151 | 0.0175 | 0.1322 |
| 4. | 0.1108 | 0.2215 | 0.0059 | 0.0005 | 0.0131 | 0.4134 | 0.0218 | 0.1476 |
| 5. | 0.1105 | 0.2207 | 0.0069 | 0.0005 | 0.0133 | 0.4132 | 0.0221 | 0.1486 |
| 6. | 0.1062 | 0.2122 | 0.0067 | 0.0004 | 0.0142 | 0.4138 | 0.0261 | 0.1616 |
| 7.* | 0.1045 | 0.2090 | 0.0038 | 0.0005 | 0.0145 | 0.4139 | 0.0280 | 0.1674 |
| 8. | 0.0974 | 0.1946 | 0.0064 | 0.0005 | 0.0163 | 0.4145 | 0.0368 | 0.1917 |
| 9.* | 0.0929 | 0.1858 | 0.0042 | 0.0004 | 0.0175 | 0.4148 | 0.0440 | 0.2098 |
| 10. | 0.0925 | 0.1849 | 0.0059 | 0.0004 | 0.0177 | 0.4158 | 0.0444 | 0.2108 |
| 11. | 0.0889 | 0.1773 | 0.0066 | 0.0005 | 0.0185 | 0.4157 | 0.0512 | 0.2263 |
| 12. | 0.0886 | 0.1769 | 0.0068 | 0.0008 | 0.0186 | 0.4157 | 0.0518 | 0.2277 |
| 13.* | 0.0843 | 0.1686 | 0.0036 | 0.0003 | 0.0198 | 0.4164 | 0.0616 | 0.2482 |
| 14. | 0.0831 | 0.1662 | 0.0059 | 0.0006 | 0.0202 | 0.4165 | 0.0639 | 0.2527 |
| 15.* | 0.0793 | 0.1592 | 0.0034 | 0.0004 | 0.0217 | 0.4171 | 0.0739 | 0.2719 |
| 16. | 0.0770 | 0.1537 | 0.0061 | 0.0003 | 0.0220 | 0.4175 | 0.0814 | 0.2854 |
| 17.* | 0.0749 | 0.1508 | 0.0038 | 0.0003 | 0.0226 | 0.4181 | 0.0872 | 0.2947 |
| 18. | 0.0752 | 0.1500 | 0.0063 | 0.0006 | 0.0225 | 0.4181 | 0.0875 | 0.2958 |

** All units are volts except ionic strength and $\sqrt{\text{ionic strength}}$.

* These solutions were made from stock solution 2.

Table 4, cont.**

| | $0.05915 \log m_{H^+}$ ($H_2$ electrode) | $2 \cdot 0.05915 \log m_{H^+}$ (solution) | $\frac{0.05915}{2} \log \frac{m_{U^{4+}}}{m_{UO_2^{2+}}}$ | $0.05915 \log R_{H_2}$ | $0.05915 \log \gamma_{H^+}$ | $E^0$ | ionic strength | $\sqrt{\text{ionic strength}}$ |
|---|---|---|---|---|---|---|---|---|
| 19.* | 0.0706 | 0.1412 | 0.0039 | 0.0004 | 0.0239 | 0.4193 | 0.1051 | 0.3241 |
| 20.* | 0.0670 | 0.1336 | 0.0072 | 0.0004 | 0.0250 | 0.4202 | 0.1202 | 0.3467 |
| 21. | 0.0667 | 0.1332 | 0.0060 | 0.0003 | 0.0251 | 0.4205 | 0.1213 | 0.3483 |
| 22.* | 0.0649 | 0.1295 | 0.0071 | 0.0005 | 0.0256 | 0.4207 | 0.1305 | 0.3613 |
| 23.* | 0.0640 | 0.1279 | 0.0034 | 0.0008 | 0.0260 | 0.4199 | 0.1361 | 0.3689 |
| 24.* | 0.0634 | 0.1268 | 0.0042 | 0.0006 | 0.0262 | 0.4212 | 0.1389 | 0.3727 |
| 25. | 0.0598 | 0.1194 | 0.0060 | 0.0004 | 0.0275 | 0.4223 | 0.1585 | 0.3982 |
| 26.* | 0.0566 | 0.1170 | 0.0040 | 0.0001 | 0.0271 | 0.4228 | 0.1683 | 0.4103 |
| 27. | 0.0546 | 0.1088 | 0.0066 | 0.0001 | 0.0295 | 0.4238 | 0.1951 | 0.4418 |
| 28. | 0.0542 | 0.1079 | 0.0068 | 0.0006 | 0.0298 | 0.4242 | 0.1984 | 0.4454 |
| 29.* | 0.0520 | 0.1040 | 0.0040 | 0.0003 | 0.0308 | 0.4247 | 0.2169 | 0.4657 |
| 30. | 0.0495 | 0.0986 | 0.0065 | 0.0002 | 0.0317 | 0.4255 | 0.2379 | 0.4873 |
| 31.* | 0.0462 | 0.0922 | 0.0040 | 0.0002 | 0.0330 | 0.4263 | 0.2718 | 0.5213 |
| 32. | 0.0423 | 0.0843 | 0.0070 | 0.0003 | 0.0341 | 0.4281 | 0.3147 | 0.5610 |
| 33.* | 0.0422 | 0.0848 | 0.0034 | 0.0004 | 0.0341 | 0.4274 | 0.3149 | 0.5611 |
| 34. | 0.0404 | 0.0806 | 0.0060 | 0.0006 | 0.0344 | 0.4278 | 0.3384 | 0.5817 |
| 35.* | 0.0345 | 0.0690 | 0.0042 | 0.0004 | 0.0360 | 0.4288 | 0.4273 | 0.6358 |

** All units are volts except ionic strength and $\sqrt{\text{ionic strength}}$.

* These solutions were made from stock solution 2.

to unity, and the value of $\frac{0.05915}{2} \log \frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}}$ becomes equal to zero.

A plot of the value of $E^{\circ\prime}$ against the ionic strength is shown in Plate 1. The extrapolated value of $E^{\circ\prime}$ to zero ionic strength gives the value of $E^{\circ}$ as 0.4117 volts.

Plate 2 shows the plot of $E^{\circ\prime}$ against the square root of the ionic strength. The decrease in slope at low and high concentrations is probably caused by the uneven variation of the two salts from the Debye Huckel limiting law. The value of $E^{\circ}$ obtained from the plot $E_o'$ against the square root of the ionic strength is less exact than that from the plot of $E^{\circ\prime}$ against the ionic strength for two reasons; first the measured values of $E^{\circ\prime}$ do not approach the vertical axis as close as in the plot using ionic strength; second, the slope changes very rapidly when the square root of the ionic strength approaches zero. For these reasons the plot of $E^{\circ\prime}$ against the ionic strength was used in preference to that against the square root of the ionic strength. The value of the standard potential of the uranous-uranyl redox electrode was found to be 0.4117 volts using this curve.

Representing the uranous-uranyl half cell as it is represented in the Critical Tables (5):

$$UO_2SO_4 + 4H^+ + SO_4 = + 2e = U(SO_4)_2 + 2H_2O.$$

$$E^{\circ} = 0.4117 \text{ volts}$$

The value of the standard potential allows the calculation of the equilibrium constant and the standard free energy change by use of equations (22) and (6) respectively. The value of the equilibrium constant is $8.34 \times 10^{19}$ and the value of the standard free energy change is -18,990 calories.

By equation (5) the values of the free energy changes were calcu-

PLATE I.

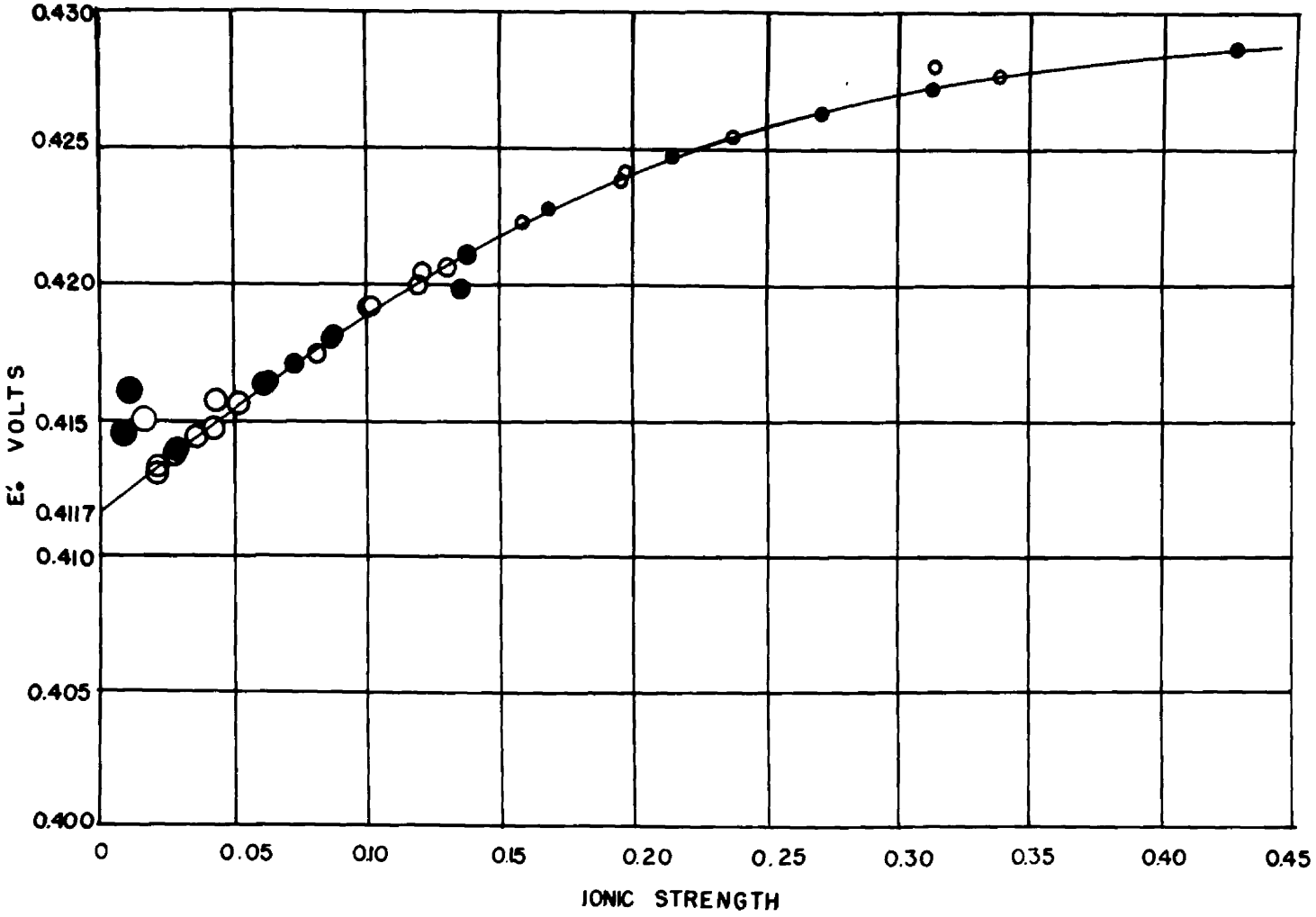
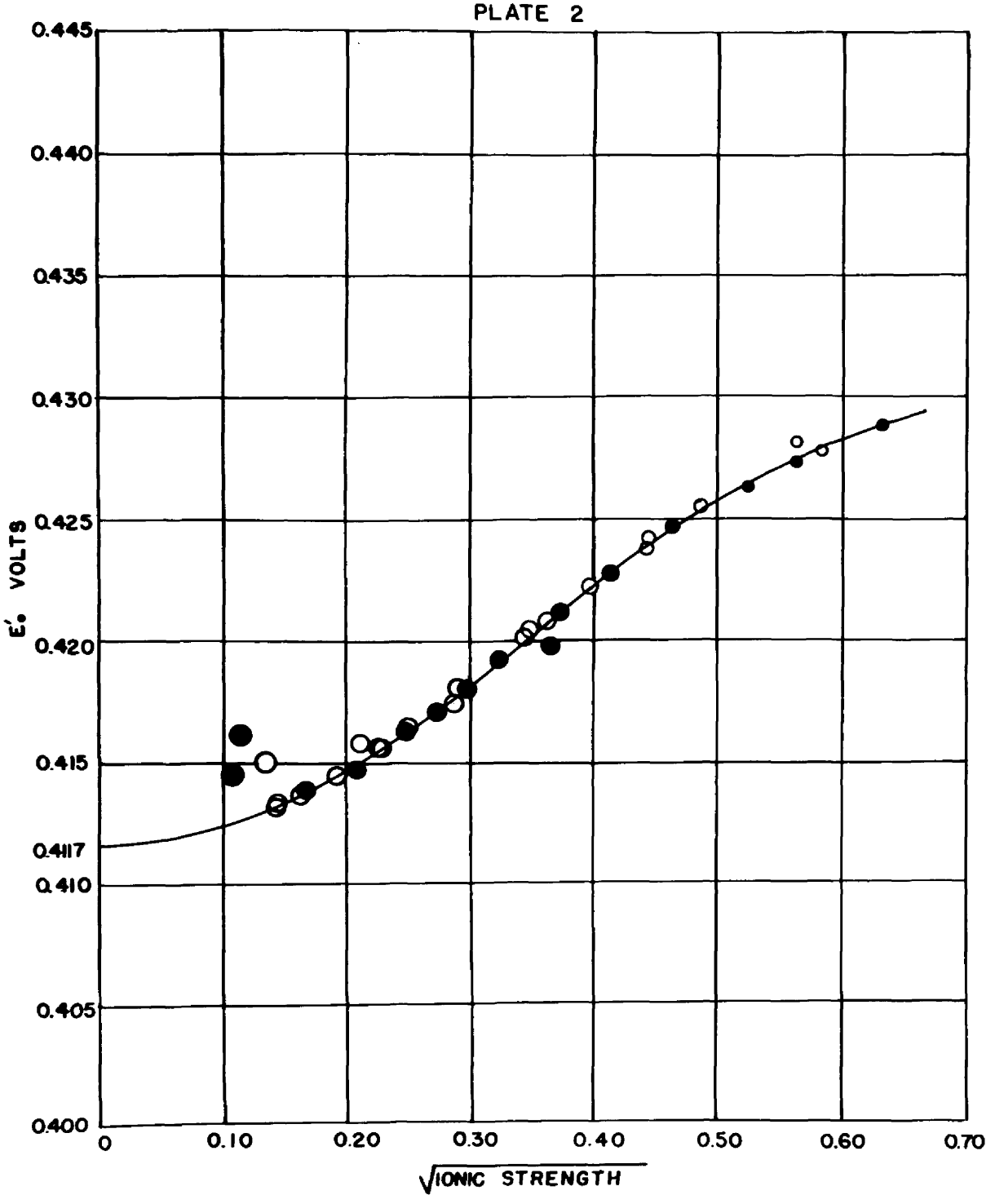

0.430
0.425
0.420
0.415
0.4117
0.410
0.405
0.400
E' VOLTS
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
IONIC STRENGTH

PLATE 2


0.445
0.440
0.435
0.430
0.425
0.420
0.415
0.4117
0.410
0.405
0.400
E'o VOLTS
0
0.10
0.20
0.30
0.40
0.50
0.60
0.70
√IONIC STRENGTH

lated from the measured potentials. Not all the measurements were used to calculate the free energy, but measurements at various well distributed ionic strengths that lay close to the curve were chosen.

These same measured potentials were used to calculate the ratio of the activity coefficients from equation (23). These results and the results of the free energy change are shown in table 5.

Table 5.

| | ionic strength $\mu$ | Meas. potential in volts | Free energy change in Kcals | $\frac{\gamma_{U^{4+}}}{\gamma_{UO_2^{2+}}}$ |
|---|---|---|---|---|
| 1. | 0.0 | 0.4117* | -18.99** | 1. |
| 2. | 0.0221 | 0.2961 | -13.66 | 0.897 |
| 3. | 0.0368 | 0.3069 | -14.15 | 0.804 |
| 4. | 0.0512 | 0.3149 | -14.52 | 0.733 |
| 5. | 0.0739 | 0.3185 | -14.68 | 0.657 |
| 6. | 0.0875 | 0.3265 | -15.06 | 0.608 |
| 7. | 0.1051 | 0.3283 | -15.14 | 0.553 |
| 8. | 0.1305 | 0.3371 | -15.55 | 0.496 |
| 9. | 0.1585 | 0.3408 | -15.72 | 0.438 |
| 10. | 0.2169 | 0.3456 | -15.94 | 0.363 |
| 11. | 0.2718 | 0.3509 | -16.18 | 0.321 |
| 12. | 0.3384 | 0.3587 | -16.54 | 0.286 |
| 13. | 0.4273 | 0.3621 | -16.70 | 0.264 |

* The value of the standard potential.

** The value of the standard free energy change.

## DISCUSSION OF RESULTS

### Errors

Potential measurements were made to the hundredth of a millivolt but were rounded off to the nearest tenth of a millivolt. The Weston Standard Cell used was calibrated to the hundredth of a millivolt; hence, it was far within the limits of experimental error.

The temperature of the water thermostat bath was 24.92° ± 0.02°C as measured with a Beckman thermometer which had been compared to a thermometer calibrated by the Bureau of Standards. Luther and Michie (3) measured the temperature coefficient of the cell:

$$\mathrm{Pt} \;\Big|\; \begin{matrix} \mathrm{U(SO_4)_2} & (ym) \\ \mathrm{UO_2SO_4} & (ym) \\ \mathrm{H_2SO_4} & (xm) \end{matrix} \;\Big|\; \mathrm{H_2SO_4}\ (xm) \;\Big|\; \mathrm{Hg_2SO_4} \;\Big|\; \mathrm{Hg}$$

and found that the temperature coefficient of the cell composed of a 1: 1 ratio of uranyl and uranous salts was 0.0005 volts per degree centigrade. L. J. Bercher and G. D. Howell (1) reported that the temperature coefficient of the cell,

$$\mathrm{Pt} \;\Big|\; \mathrm{H_2} \;\Big|\; \mathrm{H_2SO_4} \;\Big|\; \mathrm{Hg_2SO_4} \;\Big|\; \mathrm{Hg}$$

was, $\frac{dE}{dT} = 0.00027$ volts.

From these two temperature coefficients the error caused by a temperature variation of 0.1°C is well within experimental error. This can be further confirmed by calculations from equation (7). It shows that the temperature coefficient of the cell used in this experiment should be about 0.00002 volt per 0.1°C.

The weights used were calibrated by the Richards' counterpoise method (22) and were standardized with a weight standardized by the

Bureau of Standards. For the preparation of the solutions the weights used were found to be in error less than 1 part in a 1000 so that uncorrected weights were taken. The most dilute solution was prepared with an accuracy of about 0.1%, and the more concentrated solutions with even less error.

The hydrogen electrodes were used to check each other and always agreed within 0.00005 volt. The four redox electrodes checked themselves within ±0.0001 volt in concentrated solutions. The deviation of the measurements became greater with decreasing ionic strength until the measurements made in very dilute solutions had an error of ±0.0007 volt. The increasing size of the circles with decreasing ionic strength in plates 1 and 2 is an attempt to show the increasing deviation of the results with decreasing ionic strength. The value for the measurement of the standard electrode potential of uranyl sulfate and uranous sulfate in sulfuric acid with the above deviation is 0.4117 ± 0.0007 volt.

The check in results between the two stock solutions prepared was extremely good. In three instances solutions of very nearly the same concentration were prepared from both stock solutions. The check between them was well within experimental error.

Traces of oxygen have a serious effect on dilute solutions of uranyl-uranous salt mixtures. It was necessary to take precautions to remove as much oxygen as possible from the solutions prepared. In spite of the precautions taken, there remained some residual oxygen adhering to glassware and electrodes, and some undoubtedly remained dissolved in the water. This small amount of oxygen had no effect on the concentrated solutions, but the effect became more serious as the solutions were diluted. As a result, the checks between the two half cells and four

electrodes was not so good in dilute solutions. It was noted that when a cell containing a solution less than 0.0001 molal in uranous sulfate was made up rapidly with electrodes which had been used several times, the error was not so great as when the solution was allowed to stand in the mixing flask for several hours. It was thought that the solutions had not had time enough to completely react with all of the oxygen adhering to the walls of the mixing flask, and that most of the oxygen adhering to the electrodes had been displaced. Not only were the results obtained in these dilute solutions not reproduceable, but many electrodes never came to what appeared to be an equilibrium value. The potential of the cells drifted slowly, and the values of the four electrodes differed widely. For these reasons the results below 0.0001 molal salt concentration that finally gave a value that seemed to be steady were ignored in drawing the curve.

There is also a possibility that the electrodes were behaving as hydrogen electrodes in these very dilute solutions since the electrodes were saturated with hydrogen in order to remove any chlorine that may have formed during their plating. This is not very probable since the freshly plated electrodes were always used in a concentrated cell first of all and allowed to go to equilibrium there. Any hydrogen present should have diffused off during the repeated evacuation of the cell, and any remaining hydrogen must have been displaced by or must have reacted with the uranium salts.

In some instances errors were made by improper additions of water to the acid, and a solution resulted of slightly different acid concentration than the uranium solution. The liquid junction potential caused by this discrepancy was calculated by means of the Lewis and

Sargent equation (16):

$$E_L = \frac{RT}{F} \ln \frac{\Lambda'}{\Lambda''}$$

where $\Lambda'$ and $\Lambda''$ are the equivalent conductances of the two acid solutions. In every instance the error due to a liquid junction potential was found to be far less than the experimental error.

The activity coefficient of water in the dilute solutions was essentially equal to 1. The error caused by ignoring the activity coefficient of water in the most concentrated solution used is 0.00005 volts and the error decreases as the concentration decreases.

The activity coefficients of Harned and Hamer (10) for sulfuric acid read from the chart prepared from their data were made with about 0.2 to 0.3% error; nevertheless, the results obtained were much better than if the activity coefficient of sulfuric acid had been considered an unknown quantity in equation (17). The slope of the curve of the right side of equation (17) plotted against the ionic strength is changing rapidly and is approaching a large number as the ionic strength approaches zero; hence, the exact intercept is very difficult to determine. An error of 0.3% in reading the activity coefficient of sulfuric acid causes an error of about 0.0001 volts so that the standard potential can be corrected to 0.4117 $\pm$0.0008 volts.

## SUMMARY

1. A short history of previous work on the oxidation and reduction potentials of uranous and uranyl salts in acid is given.

2. The principles of the present work are treated theoretically.

3. The preparation of uranyl sulfate and uranous sulfate is discussed. The effect of air on a uranous sulfate solution is shown to be more pronounced in the presence of uranyl ion.

4. From a plot of the potentials of cells corrected for molalities of ions, gas pressure, and activities of hydrogen ions against ionic strength, the standard potential of the uranous sulfate, uranyl sulfate, sulfuric acid half cell is found to be 0.4117 $\pm$0.0008 volts when the curve is extrapolated to zero ionic strength.

5. The standard free energy change and equilibrium constant are calculated to be -18,990 calories and $8.34 \times 10^{13}$ respectively.

6. The free energy change of the half cell reaction and the ratio of the activity coefficients at various concentrations are calculated.

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